DELINEATION OF A HYDROCARBON (WEATHERED GASOLINE) PLUME IN SHALLOW DEPOSITS AT THE U.S. NAVAL WEAPONS STATION, SEAL BEACH, CALIFORNIA

By Roy A. Schroeder

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 89-4203

Prepared in cooperation with the

U.S. DEPARTMENT OF THE NAVY

5018-19

U.S. DEPARTMENT OF THE INTERIOR MANUEL LUJAN, JR., Secretary

U.S. GEOLOGICAL SURVEY Dallas L. Peck, *Director*



Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

For sale by the Books and Open-File Reports Section, U.S. Geological Survey Federal Center, Box 25425 Denver, CO 80225

For additional information write to: District Chief U.S. Geological Survey Federal Building, Room W-2234 2800 Cottage Way Sacramento, CA 95825

CONTENTS

Abstract 1

Introduction 1

Background 1

Purpose and scope 1

Location of the study area 2

Physiographic and hydrogeologic setting 3

Data collection and analysis 4

Site selection and well installation 4

Data- and sample-collection methods 7

Soil cores 7

Ground-water levels 8

Ground-water quality 8

Analytical methods 8

Hydrocarbons in soil cores 8

Ground-water analyses 9

Hydrogeology 9

Hydrogeology of the shallow subsoil 9

Effect of marsh on inorganic quality of ground water 13

Ground-water levels and movement 13

Tidal influence on ground-water levels 13

Ground-water gradients and flow patterns 16

Delineation of hydrocarbon plume 17

Hydrocarbon concentration in soil cores 17

Possible additional source of petroleum contaminants 18

Nitrate concentration in monitor wells 20

Volatile organic compounds in monitor wells 21

Estimated quantity of gasoline in the subsoil 23

Migration and assimilation of gasoline 24

Spreading of gasoline in a porous medium 24

Natural assimilation of gasoline in subsoils 26

Summary and conclusions 27

References cited 28

FIGURES

1-3. Maps showing:

- 1. Location of study area and major geographic and physiographic features near the U.S. Naval Weapons Station, Seal Beach, California 2
- 2. Location of coastal gaps and mesas in northern Orange and southern Los Angeles Counties 3
- 3. Location of monitor wells and geologic sections in the study area 5
- 4. Generalized geologic sections 10

Figures--Continued

- 5,6. Maps showing:
 - 5. Specific conductance in monitor wells 14
 - 6. Chloride/sodium ratio in monitor wells 15
 - 7. Hydrographs showing tidal influence on water level at well 9 16
 - 8. Map showing estimated areal extent of gasoline plume in shallow subsoil 19
 - 9. Graph showing distribution of retention times during gas-chromatographic analysis of fuel standards and hydrocarbons in the study area 20
- 10. Map showing nitrate concentration in monitor wells 22

TABLES

- 1. Well-construction and synoptic water-level data 6
- 2. Particle-size distribution in soil cores from test holes 12
- 3. Hydrocarbon concentration in soil cores from test holes 18
- 4. Dichloroethane concentration in monitor wells 21
- 5. Calculated areal concentration of gasoline at test holes 23

CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL AND TIDAL DATUMS

Conversion Factors

Multiply	Ву	To obtain
acre	0.4047	square hectometer
inch (in.)	25.40	millimeter (mm)
foot (ft)	0.3048	meter
square foot (ft ²)	0.09294	square meter (m ²)
oot squared per day (ft ² /d)	0.09294	meter squared per day
mile (mi)	1.609	kilometer
gallon (gal)	3.785	liter (L)
quart	0.9464	liter (L)

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

Temp. $^{\circ}F = 1.8 \text{ temp. } ^{\circ}C + 32.$

Abbreviations

g	-	gram	GC	-	gas chromatography
mL	-	milliliter	GC-FID	-	gas chromatographic separation
g/cm ³	-	gram per cubic centimeter			with flame-ionization
kg/m ²	-	kilogram per square meter			detection
mg/kg	-	milligram per kilogram	GC-MS	-	gas chromatographic separation
mg/L	-	milligram per liter			with mass-spectrometric
$\mu g/L$	-	microgram per liter			confirmation
$\mu S/cm$	-	microsiemen per centimeter			
		at 25 degrees Celsius			

Vertical Datum

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Tidal Datum

Tides are given in feet above or below the tidal datum of the Los Angeles Outer Harbor. The tidal datum, which is the mean of the lower of the two low waters of each day over a 19-year Metonic cycle, is 2.77 feet below sea level.

DELINEATION OF A HYDROCARBON (WEATHERED GASOLINE) PLUME IN SHALLOW DEPOSITS AT THE U.S. NAVAL WEAPONS STATION, SEAL BEACH, CALIFORNIA

By Roy A. Schroeder

Abstract

Gasoline from a leaking underground storage tank at the U.S. Naval Weapons Station in Seal Beach, California, was found to have spread almost radially through the shallow subsoil a distance of 150 to 300 feet from the source. Deposits in an area of 160,000 square feet in a zone 1 to 2 feet thick above the shallow water table are contaminated.

Seasonal and tidal fluctuations in ground water have spread the gasoline vertically in the subsoil and thereby reduced gasoline concentration below residual saturation in nearly all the contaminated area. Total quantity of gasoline contained in gasoline-unsaturated subsoil is estimated to be 5,800 gallons. The quantity present in gasoline-saturated subsoils was not determined.

INTRODUCTION

Background

In early 1984, during an evaluation of subsoil properties prior to installation of new fiberglass fuel-storage tanks at the U.S. Naval Weapons Station, Seal Beach, California (Seal Beach Naval Weapons Station), an existing 12,000-gallon steel underground storage tank was found to have leaked gasoline (Lee and Ro Consulting Engineers, 1984). Use of the tank was immediately discontinued. The gasoline poses no threat to present drinking-water wells because none exist in the study area. There is concern, however, that the gasoline might contaminate a nearby tidal marsh that is part of

the Seal Beach National Wildlife Refuge. Because of the potential adverse effect on the refuge, the Navy requested that the U.S. Geological Survey assess the extent of contamination from the gasoline leak. Prior to this study, base personnel estimated a loss of 2,000 gal of gasoline; they noted, however, that it was impossible, using available delivery and sales records at this large-volume service station, to define precisely either the timing or quantity of the leakage (S. Sunderland, Seal Beach Naval Weapons Station, oral commun., 1984).

Purpose and Scope

The purpose of this study, done in cooperation with the U.S. Department of the Navy, was to delineate an area contaminated by gasoline at the Seal Beach Naval Weapons Station, thereby providing the Navy with information that could be used in developing plans to mitigate the effects of gasoline contamination at the site. This report contains information on lithologic properties obtained during boring of 33 shallow test holes, as well as hydrologic information obtained from monitor wells that were installed in the 33 test holes. Vertical and horizontal extent of the gasoline plume in the shallow subsoil was determined from field observations of gasoline odor and change in soil color, and from chemical analysis of soil cores taken during augering of the test holes.

This study was formally completed in 1985; however, sparse information indicating a possible leak of diesel fuel or a similar petroleum distillate (another source), in addition to the known gasoline leak, became available in 1986 and is included in this report. Also subsequent to completion of the study, it was indicated that the known leak was in fact leaded gasoline (V. Novstrup, Naval Energy and Environmental Support Activity, Port Hueneme, written commun., 1989; Naval Energy and Environmental Support Activity, 1985) rather than unleaded gasoline as originally indicated.

Location of the Study Area

The U.S. Naval Weapons Station at Seal Beach, California, is in coastal northern Orange County (fig. 1). The city of Seal Beach is surrounded by the cities of Long Beach (in Los Angeles County), Los Alamitos, Garden Grove, Westminster, and Huntington Beach and by the Pacific Ocean to the southwest. The Seal Beach National Wildlife Refuge, which is contained entirely within the Seal Beach Naval Weapons Station, is a tidal marsh connected to the ocean by Anaheim Bay.

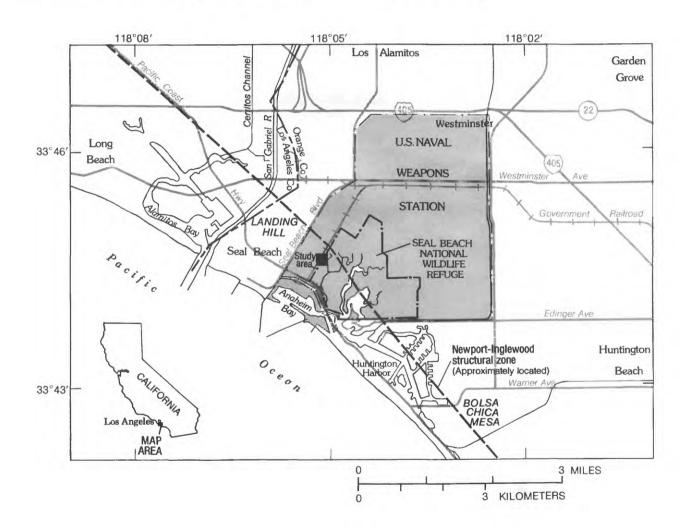
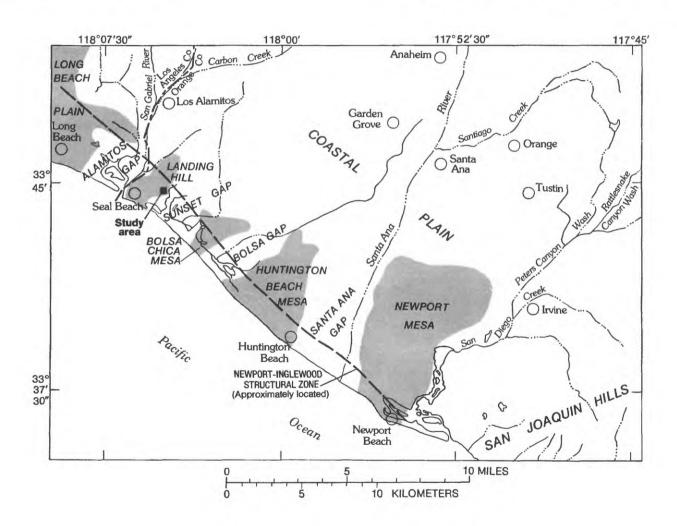


Figure 1. Location of study area and major geographic and physiographic features near the U.S. Naval Weapons Station, Seal Beach, California.

Physiographic and Hydrogeologic Setting

The approximately 10-acre study area, which consists of a low terrace on the west side and part of a marsh on the east side, is in Sunset Gap. Sunset Gap is between Landing Hill and Bolsa Chica Mesa (figs. 1 and 2), on the western edge of the coastal plain of Los Angeles and Orange Counties. Geologic lithology, and hydrogeology of Sunset Gap have been described by Wall and others (1967), and by others in reports referenced therein, and are briefly summarized below.

The western edge of the coastal plain in Orange County is characterized by a succession of low hills and mesas that are about 1 to 3 mi inland of the Pacific Ocean. These low hills and mesas are the land-surface expression of a series of northwest-trending anticlinal folds and faults known as the Newport-Inglewood structural zone. The structural zone has been transected by six gaps through which alluvium of the coastal plain extends to the coast. These gaps are the result of stream erosion--except for Sunset Gap, which is a structural downwarp. The shallow sediments beneath the gaps are



Location of coastal gaps and mesas in northern Orange and southern Los Angeles Figure 2. Counties.

more permeable than the sediments beneath the mesas. The location of gaps and mesas near the study area is shown in figure 2.

Deposits have accumulated on the surface of the downwarp in Sunset Gap, during the Holocene Epoch, to a thickness of about 30 to 35 ft. These shallow deposits were transported by floodwaters from streams that normally discharged through adjacent gaps, by flow in temporary channels, and by wave action resulting from high-intensity storms. Floodflow now is largely controlled by levees and flood-control channels. The sediments that compose the shallow deposits contain minor amounts of gravel, but particle size generally ranges from clay to coarse sand. Much of this material has been reworked by tides and floods, resulting in interfingering lenses of sand, silt, and clay; thus, correlation of lithologic units can be made only for very short distances.

Underlying the thin veneer of surficial Holocene deposits are deposits of Pleistocene and late Pliocene age that contain the main body of freshwater in the coastal plain. These deeper, mostly unconsolidated deposits consist of interfingering lenses of sand, silt, and clay. Although these deposits are a source of potable water throughout the coastal plain, no public-supply wells exist near the study area. In the study area, these deposits are about 2,000 ft thick. In Sunset Gap, no continuous low-permeability layers separate the main body of freshwater from the overlying shallow deposits.

Consolidated rocks of Tertiary age underlie the main body of freshwater and form the base of the freshwater aquifer. These rocks are mainly sandstone, siltstone, and conglomerate of low permeability. In most of the coastal plain, these rocks contain saline water.

Regional maps showing the distribution of sediment types and transmissivities in the upper 100 ft of the deposits in Sunset Gap were prepared by Wall and others (1967). For the

upper 25 ft of deposits, the maps indicate about equal areas of predominantly sandy silt with transmissivity of 0.33 to 3.3 ft²/d and silty sand with transmissivity exceeding 3.3 ft²/d--along with silty clay with transmissivity less that 0.33 ft²/d in about 10 percent of the area. Only the extreme southwestern part of the study area (near test wells 7 and 13, fig. 3) is within the zone of silty clay; most of the study area contains silty sand with transmissivity exceeding 3.3 ft²/d. The regional maps indicate that deposits become coarser with increasing depth. Between 75 and 100 ft below land surface, about 90 percent of Sunset Gap contains predominantly silty sand with transmissivity exceeding 3.3 ft²/d.

DATA COLLECTION AND ANALYSIS

Site Selection and Well Installation

To determine the local geohydrology and the extent of contaminant migration, 33 test holes were drilled and monitor wells were installed by the U.S. Geological Survey in 1984 and 1985. The test holes and monitor wells are numbered consecutively from 2 through 34 in order of their installation and are shown in figure 3. Two preexisting steel wells (given local well numbers 1 and 1A) near monitor well 5 and next to the railroad also are shown in figure 3. Although the preexisting wells were used to obtain preliminary information prior to test-hole drilling, their perforated intervals were unknown and the wells were obviously damaged; therefore, no data from those wells are included in this report.

Test holes 2-5 were drilled in September 1984 with a 2-inch-diameter manually operated auger. The holes were used primarily to obtain preliminary lithologic, water-level, and water-quality information prior to extensive drilling that delineated precisely the area and depth of contamination. Holes 6-24 were drilled in November 1984 with a 6-inch-diameter truck-mounted hollow-stem auger and were used to

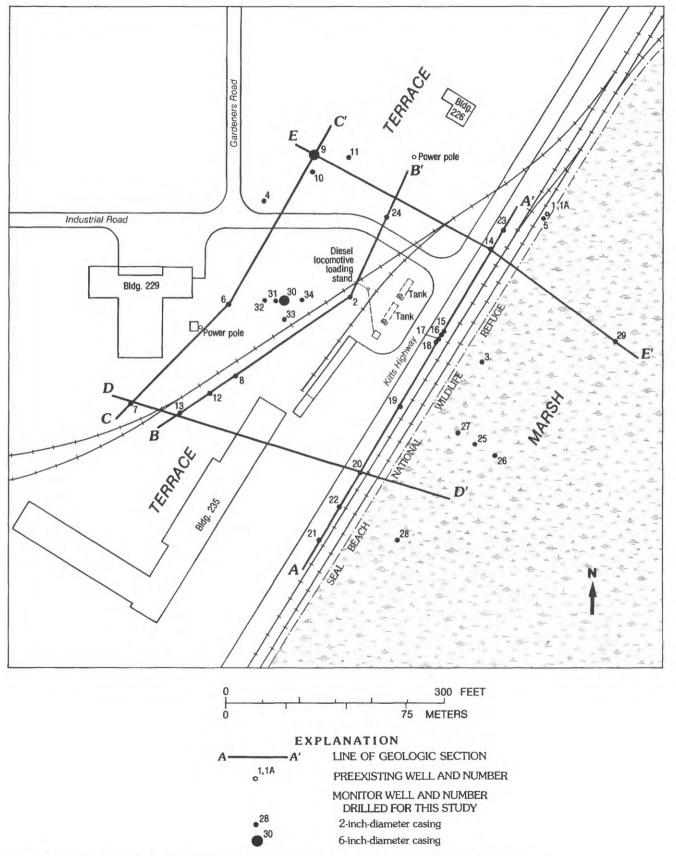


Figure 3. Location of monitor wells and geologic sections in the study area.

delineate contaminated deposits in the terrace. Holes 25-29 were drilled in December 1984 to a depth of 3 ft below land surface using a 4-inch-diameter handheld power auger and then to about 5 ft below land surface using a 2-inchdiameter manually operated auger; these holes were used to delineate contaminated deposits in the marsh. Hole 30 was drilled in July 1985 with a 10.5-inch-diameter truck-mounted hollow-stem auger, and holes 31-34 were drilled in July 1985 with a 6-inch-diameter truckmounted hollow-stem auger. Wells installed in holes 30-34 were to be used for contaminantrecovery and tracer-injection tests; however. problems with installation of the large-diameter well 30 (collapse of native material into the hole during well installation) and restrictions on well development (a result of prohibitions on surface disposal of the slightly contaminated water that would be generated) precluded these Only qualitative observations were obtained from holes 30-34.

Dedicated auger flights, not previously used in the contaminated area, were used to drill holes in uncontaminated soils; and all auger flights used for drilling into contaminated soils were cleaned with hot water and soap at a commercial car wash before reuse. No grease was used in connecting the 5-foot auger flights.

Two-inch-diameter Schedule 40 PVC (polyvinyl chloride) casing was installed in all test holes except holes 9 and 30, where 6-inch-diameter PVC casing was used. The 2-inch PVC pipe is slotted with three rows of 0.020-inch horizontal openings about 0.3 in. apart; the 6-inch PVC pipe has eight rows of slots. Depth of the perforated (slotted) interval for each well is given in table 1. The casing was purchased in 20-foot continuous sections slotted commercially

Table 1. Well-construction and synoptic water-level data

[Water levels measured during 1-hour period January 12, 1985. Altitudes, perforated intervals, and water levels in feet; LSD, land-surface datum; --, data not obtained]

Local	Altitude of	Perforated	Wate	r level
well No.	land surface (above sea level)	interval (below LSD)	(below LSD)	(above sea level)
1	9.21	12		-1
1A	9.28			
2	9.06	5.8-10.3	7.35	1.71
3	4.36	1.3-6.3	2.73	1.63
4	8.72	3.1-12.5	7.02	1.70
5	9.31	4.2-8.8	7.70	1.61
6	10.06	4.1-14.1	8.34	1.72
7	9.34	3.5-13.5	7.66	1.68
8	8.63	3.8-13.8	6.94	1.69
9	9.52	3.7-17.7		
10	12.16	7.8-17.8	10.53	1.63
11	12.42	4.0-14.0	10.85	1.57
12	8.38	1.5-11.5	6.71	1.67
13	8.41	3.2-13.2	6.73	1.68
14	8.81	3.9-13.9	7.14	1.67
1.5	8.33	10.3-11.3	6.65	1.68
16	8.38	16.0-17.0	6.71	1.67
17	8.47	5.9-8.9	6.81	1.66
18	8.37	4.2-14.2	6.74	1.63
19	8.44	2.4-12.4	6.77	1.67
20	8.48	2.7-12.7	6.84	1.64
21	8.52	2.6-12.6	6.85	1.67
22	8.67	2.5-12.5	6.99	1.68
23	9.13	3.0-13.0	7.49	1.64
24	8.57	1.7-11.7	6.92	1.65
25	3.91	1.5-5.0	2.58	1.33
26	3.58	1.5-5.0	2.29	1.29
27	4.14	1.9-5.4	2.62	1.52
28	4.22	1.8-5.3	2.67	1.55
29	3.26	1.5-5.0	1.99	1.27
30		1.0-15.0		
31	4-	4.5-14.5		1.44
32	22	5.0-15.0	1-4	
33		4.2-14.2		
34		5.0-15.0		

by machine at one end. Because total well depths generally were less than the length of the casing, few of the wells contain casing with joints where sections are pieced together. Where more than one section was used, they were either threaded together or joined using metal screws (no glue was used). The annular space between the casing and borehole walls was filled with clean quartz sand in all except the 2-inch-diameter holes. In the 2-inch holes, the casing fit flush with the borehole, and thus no annulus existed. The 2-inch wells were developed by pumping and by air-surging.

All wells, except those in the marsh (wells 3 and 25-29), were sealed at the surface with concrete. Well 3 at the western edge of the marsh, a 2-inch borehole fitted with a 2-inch casing, had no annulus and therefore was not sealed. Wells 25-29 were sealed to within 6-8 in. below land surface with bentonite pellets. Evidence that the seal may leak in wells 25-29 comes from a comparison of ammonium concentrations in the wells to concentrations in the marsh. Measured concentrations in wells 25-29 were about half the value of 0.4 mg/L as NH₄-N (ammonium as nitrogen) for surface seawater in the marsh and much greater than the concentration of about 0.01 mg/L found for well 3 in the marsh and for all wells in the terrace.

Holes 15-18, at the eastern edge of the terrace (fig. 3), were drilled adjacent to one another so that information could be obtained on the variability of chemical analyses from apparently identical deposits. Each monitor well installed in these test holes was perforated at a different depth so that any vertical variation of water quality below the water table could be determined. Wells 15 and 16 were sealed

immediately above and below the 1-foot slotted interval in the saturated zone with bentonite pellets.

Data- and Sample-Collection Methods

SOIL CORES

Soil cores were taken from selected depths with an 18-inch split-spoon sampler in test holes 6-24 (accuracy approximately 1 ft relative to land surface) drilled with a hollow-stem auger. (Location of test holes is shown in fig. 3.) Descriptive lithology was recorded from the cores, and selected samples were analyzed for particle size and for hydrocarbon concentration. Soil-core samples from holes 6, 12, 14, and 24 were sent to the U.S. Geological Survey's Sediment Laboratory in Salinas, California, for determination of particle-size distribution using methods described by Guy (1969).

The outer part of the core, where it is in contact with the steel wall of the split spoon, was scraped away and discarded. The remaining soil from the interior part of the core was placed in a 1-quart glass jar with Teflon-lined screw cap and stored on ice. The sample was shipped, chilled on ice, for gas-chromatographic analysis at the U.S. Geological Survey Laboratory in Arvada, Colorado. The split-spoon sampler was cleaned with acetone and water prior to collection of each core.

Soil (auger cuttings) from test holes in the marsh was scraped from the blades of the power and manual augers. Although this method obviously is less accurate than coring, which recovers an entire vertical profile intact, an attempt was made to obtain soil samples representative of the entire contaminated vertical profile.

Synoptic water-level measurements were made in January and April 1985. A period of less than 1 hour was needed to complete the January synoptic measurements at all monitor wells in the study area. The results of the January measurements are given in table 1. Ground-water (or floating-fuel) levels were measured using a steel tape. Thickness of floating fuel was measured using electricalconductivity probes or bottom-filling bailers lowered slowly into the well. Altitudes of the monitoring wells were surveyed to 0.01-foot accuracy relative to Orange County survey mark #CMM S.B1, which is located within the study area on the east edge of the raised railroad bed adjacent to the marsh. Altitude of this survey marker was 8.91 ft above sea level in 1976.

In addition to the two synoptic water-level measurements made in all monitor wells at the study area, the magnitude of well-to-well variations in tidal response was ascertained from frequent water-level measurements obtained on several monitor wells during a 6-hour period (one-half tidal cycle). A continuous hydrograph was obtained from a water-level recorder mistalled on well 9.

GROUND-WATER OUALITY

Ground-water samples for chemical analysis were obtained during 1984-85 using bailers attached to a steel cable. First, three to five casing volumes of water were removed from the well with an open-top steel bailer to ensure that a representative sample of ground water was taken. Samples then were collected using a glass bailer equipped with a glass ball-check valve at the bottom. Samples were placed in appropriate containers, stored on ice, and shipped immediately to the U.S. Geological Survey Laboratory in Arvada, Colorado, for analysis.

Bailers were cleaned with detergent, acetone, and distilled water prior to collection of each ground-water sample. In addition, different (dedicated) bailers were used to sample contaminated and uncontaminated wells, thereby minimizing chances of cross-contamination, and samples were collected in approximate order from least to most contaminated (lowest to highest concentration).

Analytical Methods

HYDROCARBONS IN SOIL CORES

Core-soil samples and auger cuttings were analyzed by GC-FID (gas-chromatographic separation with flame-ionization detection) using methods described in Wershaw and others (1987). About 50 g (dry weight) of soil was extracted using a solvent mixture containing 80 mL hexane and 20 mL acetone. A known amount of eicosane, a straight-chain alkane containing 20 carbon atoms, was added prior to extraction. The eicosane was used both as an internal and surrogate standard, thus permitting calculation of total hydrocarbon concentration.

Chromatographic separation was performed using an SE-54 fused-silica capillary column 25 mm long and 0.21 mm inside diameter. The GC oven was held at 50 °C for 5 minutes following injection of the concentrated extract and programmed to increase to 300 °C at 6° per minute.

Hydrocarbon concentration is obtained by dividing total area under all the chromatographic peaks by the response factor for eicosane. The response factor is the area under the eicosane chromatographic peak per unit eicosane concentration. Whittemore (1979) identified more than 300 compounds in gasoline; nearly all are hydrocarbons containing only carbon and hydrogen atoms, and hence are expected to have response factors about equal

to that of eicosane. Therefore, the error resulting from the assumption that all hydrocarbons present in the sample have equal responses is probably minor in comparison with the errors (discussed in a later section) introduced by sample handling and natural variability. Also, minor errors may result because a few highly volatile compounds have retention times similar to the solvent and are therefore masked by the solvent. Most of the highly volatile compounds likely escaped (volatilized) from the deposits soon after the spill occurred.

In addition to GC-FID analyses done on subsoil samples from numerous test holes in the study area, GC-MS (gas-chromatographic separation with mass-spectrometric confirmation) scans for extractable priority pollutants (Keith and Telliard, 1979), as well as identifiable coelutants, were done on samples from hole 24 in the terrace deposits and hole 27 in the marsh. The primary purpose of these scans was to confirm the expected absence of organic contaminants (such as pesticides and industrial compounds) other than those normally found in refined petroleum fuels. The scans also provided quantitative information on aromatic hydrocarbons in the subsoil, as discussed in later sections of this report.

GROUND-WATER ANALYSES

Water from selected monitor wells was analyzed for selected inorganic ions and macronutrients and for purgeable organic priority pollutants.

Specific conductance was measured in the field immediately after samples were collected. Water for analysis of inorganic ions and nutrients was filtered through a cellulose-acetate membrane with nominal 0.45-micrometer pore openings. Aliquots for analysis of nutrients were preserved by addition of mercuric chloride and chilling on ice. Aliquots for analysis of inorganic

cations were stabilized by addition of nitric acid to pH less than 2. Analyses for inorganic ions and nutrients were done using procedures described by Fishman and Friedman (1989) and Feltz and others (1983).

Samples for analysis of purgeable organic compounds were shipped (chilled on ice in 40-mL glass vials with Teflon-lined septum) to the laboratory, where they were analyzed using procedures described by the U.S. Environmental Protection Agency (1979), Feltz and others (1983), and Wershaw and others (1987). Detection limit for each compound was 3 μ g/L.

HYDROGEOLOGY

Hydrogeology of the Shallow Subsoil

The raised railroad bed adjacent to Kitts Highway forms the boundary between the marsh in the eastern part of the study area and the terrace in the western part (fig. 3). Landsurface altitude of the terrace ranges generally from about 8 to 12 ft above sea level, and altitude of the marsh is about 4 ft above sea level. (See table 1.) Land-surface altitudes at the monitor wells (table 1) show that during tides exceeding about 5 ft (at the outer coastline), the entire marsh area (within the study area) is inundated by seawater.

The five generalized geologic sections for the study area (fig. 4) are based on detailed visual inspection of soil cores and auger cuttings obtained during drilling and on analysis of particle-size distribution in selected soil-core samples (table 2). Numerous thin strata (which field observations indicated to be generally only a few inches in thickness and of limited areal extent) are not depicted. The geologic sections show that a surface layer consisting of poorly sorted fine sand, silt, and clay covers the entire study area. This layer is about 6 to 8 ft thick

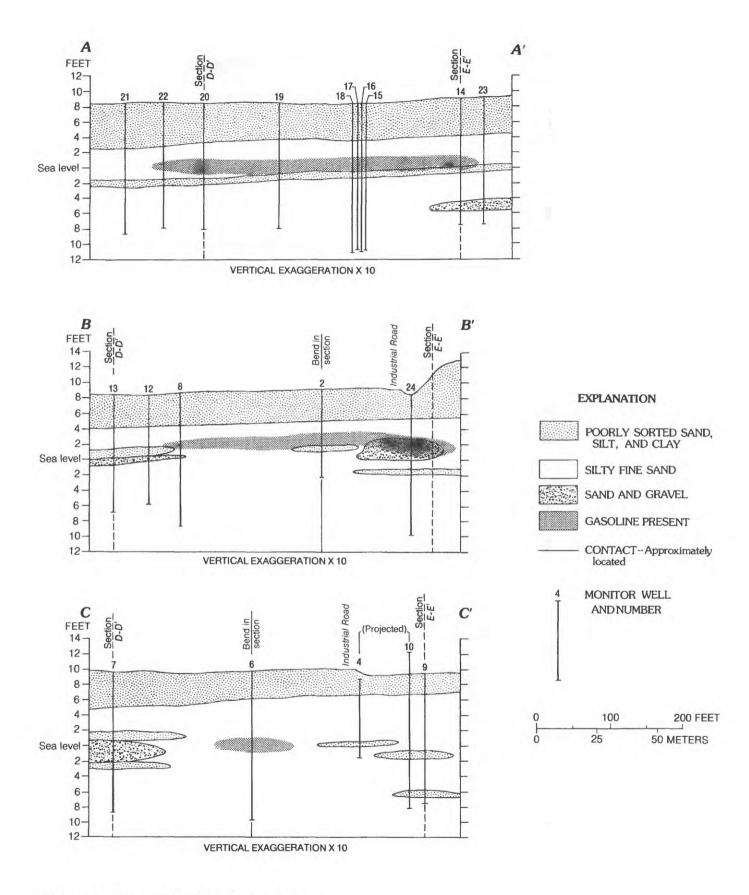
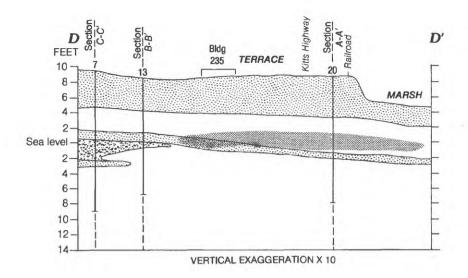
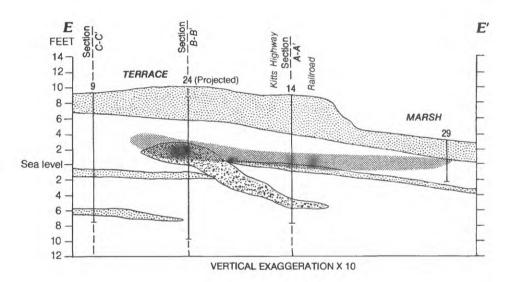


Figure 4. Generalized geologic sections.





throughout most of the area, but it decreases to about 2 ft thick in the marsh on the southeastern edge of the study area. Data in table 2 indicate equal proportions of clay, silt, and sand in this surface layer.

Below the surface layer, deposits consist of medium to fine sand and silt with only a trace of clay. In general, these deposits become coarser with increasing depth. Particle-size analysis of the soil core collected from 26 ft below land surface in hole 6 indicates that the deposits at that depth are composed primarily of coarse to medium sand. Several discontinuous lenses (less than 2 ft thick) of fine-grained material are present beneath the surface layer-especially at the water table, which is near sea level. In addition to the fine-grained lenses, occasional lenses of coarse-grained deposits were found that have no apparent pattern of deposition.

In the upper 2 ft of the marsh, deposits have been compacted as a result of regular

Table 2. Particle-size distribution in soil cores from test holes

[Expressed as weight-percent. LSD, land-surface datum; >, greater than; <, less than; --, none detected]

20.				Components, as		ctcis	
Hole No.	Depth interval (feet below LSD)	Gravel (>2)	Coarse sand (0.5-2)	Medium sand (0.25-0.5)	Fine sand (0.062-0.25)	Silt (0.004-0.062)	Clay (<0.004)
6	0.0-0.5	14	12	12	19	31	26
	1.0-1.5	1	12	12	16	23	36
	2.0-2.5	1	8	10	23	28	30
	3.0-3.5	1	8	11	10	33	37
	10.9-11.0		4	19	60	14	3
	12.4-12.5		2	11	63	19	5
	13.0-13.3		1	18	65	14	2
	15.0-15.2			1	39	52	8
	26.0-26.5		24	53	17	4	2
12	5.0-5.7		2	8	50	18	22
	5.7-6.5		3	3	18	36	40
	6.5-7.8		5	4	23	39	29
	7.8-8.8	1	34	33	20	6	6
	9.5-12.5	44	25	15	66	13	6
14	1.0-1.5	1	3	12	32	26	26
	3.0-4.5		2	10	34	26	28
	6.0-7.3		2	15	45	25	13
	7.3-8.3		3	12	24	49	12
	8.3-9.5	7	12	7	12	50	12
	9.5-10.5	2	14	6	23	46	9
	11.5-13.5	5	1	1	55	33	5
	14.2-14.7	30	10	4	11	37	8
24	6.5-8.0	1	39	35	20	3	2

inundation by the tides. Furthermore, as is typical for tidal marshes, a thin veneer of organic-rich mud covers the surface of the marsh. These deposits form a barrier of low permeability that could limit the interaction between surface water in the marsh and the gasoline-contaminated subsoil.

Effect of Marsh on Inorganic Quality of Ground Water

Seawater and dissolution of soil minerals are the principal sources of dissolved ions in ground water at the study site. The specific conductance in monitor wells is shown in figure 5. Although differences in well depth and perforated interval probably are the cause of some local variations, conductance generally increases toward the marsh.

Specific conductance in water from monitor wells 2-5 varied less than 4 percent (differences that are close to analytical precision) during a tidal cycle. Such small changes suggest that there is little horizontal variation in ground-water flow patterns in or near the marsh associated with the tides.

Chloride/sodium weight ratios in samples from wells in the study area are shown in figure 6. The chloride/sodium ratio is 1.8 in seawater. Values less than 1.8 in the ground water result from addition of sodium by dissolution of, or by ion exchange with, subsoil minerals. The ratio decreases to less than 1.8 a short distance inland from the marsh (fig. 6), indicating little interaction between ground water in the terrace and ground water or seawater in the marsh. Even the ground water in well 3 at the western edge of the marsh is only slightly saline: its specific conductance is about 6,000 μ S/cm, in comparison with about 50,000 μ S/cm for surface water in the marsh.

Ground-Water Levels and Movement

TIDAL INFLUENCE ON GROUND-WATER LEVELS

Although synoptic water-level data from monitor wells (discussed in next section) suggest that ground-water movement is from west to east, tidal influences make determination of magnitude and even direction of the hydraulic gradient imprecise. A water-level recorder installed for 2 weeks on well 9 showed a ground-water-level response of 0.2 ft to tidal changes. The hydrographs in figure 7 depict changing water level in well 9, in feet above sea level, and tides in the Los Angeles Outer Harbor. Tidal datum, which is the mean of the lower of the two low waters of each day over a 19-year Metonic cycle, is 2.77 ft below sea level (National Oceanic and Atmospheric Administration, oral commun., 1987). The location of well 9, among the farthest from the marsh, suggests that the magnitude of its tidal response might be less than that of most wells in the study area.

Periodic water-level measurements were made, with steel tapes, in several monitor wells during one 6-hour part of a tidal cycle in which amplitude of tidal fluctuation was about 4 ft (at the coast). The water-level measurements showed tidal-response fluctuations ranging from 0.14 to 0.55 ft, with no apparent relation between magnitude of the response and distance from the marsh. Not only did the monitor wells show differences in the magnitude of their tidal response, they also showed shifts between one another of as much as an hour. Such wellto-well variations in both amplitude and phase of the tidal response could be caused by localized differences in lithology, by differences in depth of the perforated interval, and by artifacts of well construction such as backfilling of the annulus and (or) incomplete development. These variations complicate preparation of water-level maps and precise calculation of

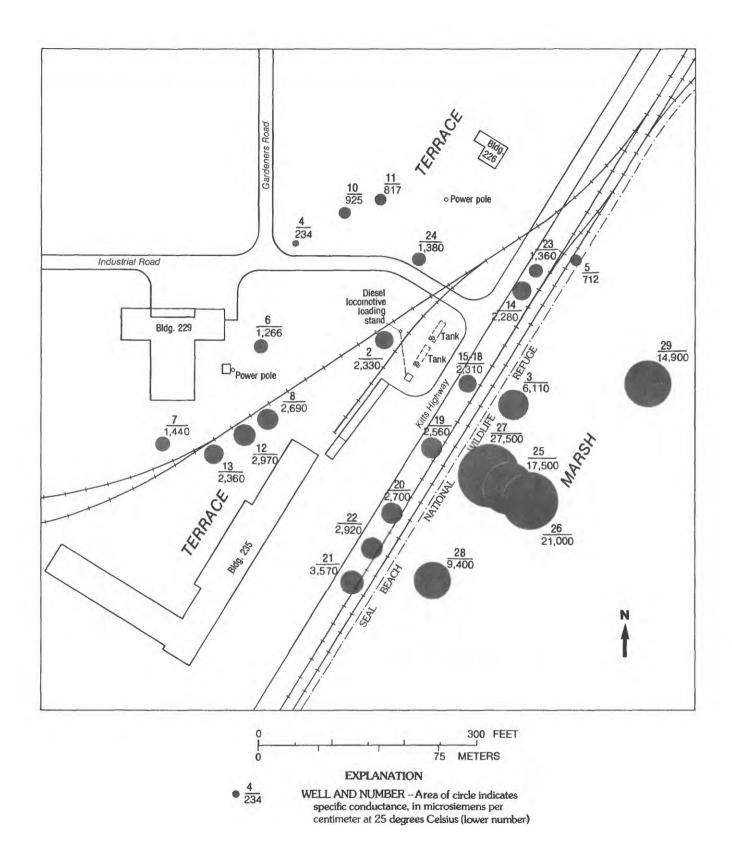


Figure 5. Specific conductance in monitor wells.

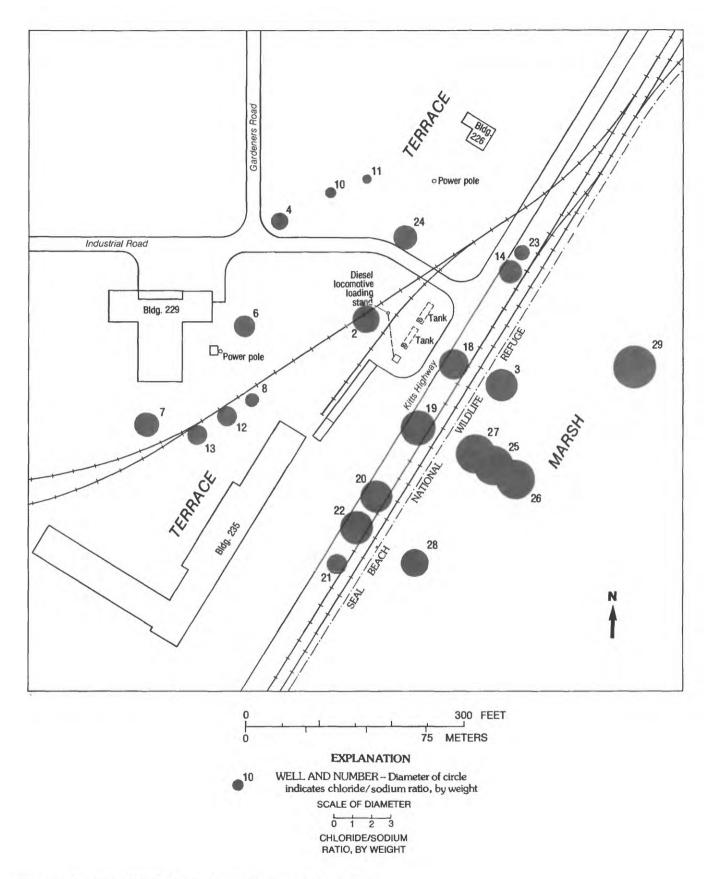


Figure 6. Chloride/sodium ratio in monitor wells.

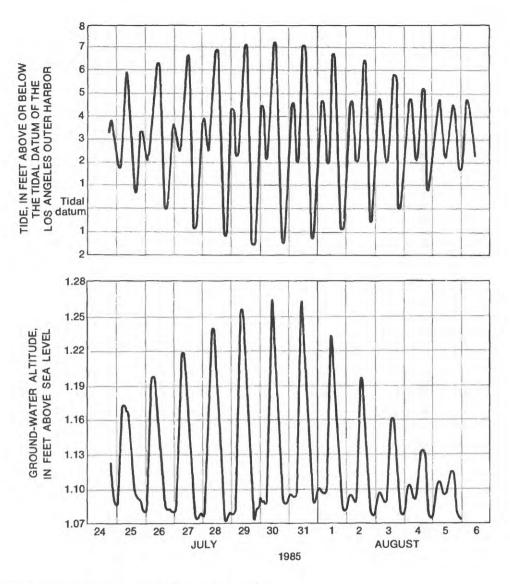


Figure 7. Tidal influence on water level at well 9.

hydraulic gradient because the gradient is so small in the study area.

GROUND-WATER GRADIENTS AND FLOW PATTERNS

Synoptic water-level measurements, to within approximately 0.01 ft, were made in January and April 1985 in order to determine the direction of ground-water movement and estimate hydraulic gradient in the study area. In January, the water levels ranged from about 1.7 ft above sea level on the west to 1.3 ft (in the marsh) on the east side of the study area (table 1). April water levels had declined slightly and ranged from about 1.3 ft above sea level on the west to

0.9 ft on the east side of the study area, maintaining a pattern similar to that in January. The drop in water levels from west to east is somewhat steeper across the terrace/marsh boundary than it is within the terrace and within the marsh. During both measurement periods, the general direction of ground-water movement was from the west toward the marsh in the east, and estimated hydraulic gradient was 1 ft per 1,500 ft. The direction of shallow ground-water movement in the study area differs from regional flow patterns, which are toward the southwest in the direction of the coast. This difference between regional and local flow patterns probably results from the presence of the marsh in the eastern part of the study area.

DELINEATION OF HYDROCARBON PLUME

The areal and vertical extent of hydrocarbon contamination has been estimated on the basis of chemical analyses of soil cores from the test holes. Water in the monitor wells is an unreliable indicator of the presence of petroleum hydrocarbons because water from many wells that were shown by soil chemical data to be in the contaminated area had little or no gasoline odor (Ineson and Packham, 1967, reported that odor threshold is 5 μ g/L for gasoline in water) and no soluble (purgeable) petroleum hydrocarbons (detection limit was 3 μ g/L in this study).

Chemical analyses of ground water and soil cores were done to estimate the extent of the zone containing petroleum hydrocarbons (weathered [that is, partially degraded] gasoline). Because simple aromatic compounds present in gasoline, such as benzene and substituted benzenes, have aqueous solubilities that exceed 1 mg/L, these compounds were expected to be present in ground water at the Seal Beach study area; however, they were not found. Low concentrations of nitrate in ground water were found to be a reliable indicator of the contaminated area. Presence in ground water of 1,2-dichloroethane also seems to be an indicator of the contaminated area. Both area and depth of contamination were precisely delineated by GC-FID analysis of soil cores.

Although color and odor were found to be reliable indicators of contaminated subsoil, a similarly reliable simple field indicator of contaminated ground water was not found. As noted above, Ineson and Packham (1967) reported that odor threshold is 5 µg/L for soluble gasoline compounds, and chemical analysis confirmed that all aqueous concentrations were below the threshold in wells within the area of the plume at the Seal Beach study area.

Hydrocarbon Concentration in Soil Cores

The vertical interval of subsoil contamination was readily recognizable in the field by gasoline odor and by change in soil color. Soil containing gasoline was gray, and uncontaminated native soil was brown. This color change occurs because microorganisms that reside in the subsoil consume oxygen, resulting in reduction of ferric oxides to ferrous sulfides, as they degrade the gasoline. Similar color changes were observed at another location in Orange County where jet fuel was present in the soil (Ehrlich and others, 1985, 1987). Color and odor were used in the field in the Seal Beach study to select core intervals for subsequent GC-FID analysis by the laboratory.

The relation between hydrocarbon concentration in subsoil and depth below land surface is given in table 3. These data indicate that background hydrocarbon concentration, on the basis of analysis of samples obtained from outside the area of the gasoline plume, ranges from about 4 to 10 mg/kg (of dry-weight soil). Concentration increases to 100 to 1,000 times this background level about 1 to 2 ft above the water table and then decreases again immediately below the water table. Such large increases above background indicate that more than 99 percent of the analyzed hydrocarbon within the subsoil results from contamination by partially degraded (weathered) gasoline or similar hydrocarbons, as noted in the next section of this report. Results of chemical analyses (table 3) and field observations cited above were used to delineate the area of the weathered-gasoline plume (shown in fig. 8).

In addition to the GC-FID analyses described above, two subsoil samples, from holes 24 and 27, were analyzed for extractable organic compounds by GC-MS. In addition to numerous alkanes, about 10 substituted benzenes and naphthalenes were identified. These aromatic compounds constituted 2 percent of the total extractable hydrocarbon at hole 24 in the

Table 3. Hydrocarbon concentration in soil cores from test holes

[Subsoil depth interval is in feet below land surface. Concentration is in milligrams per kilogram of dry soil]

Hole No.	Subsoil depth interval	Hydro- carbon concen- tration	Hole No.	Subsoil depth interval	Hydro- carbon concen- tration
6	5.0-6.0	4.2	18	6.9-7.2	16
	6.5-6.9	4.3		7.2-8.0	1,500
	6.9-7.3	7.1		8.0-9.0	390
	7.3-7.6	2,500		9.0-9.5	5.1
	8.0-8.4	32,000			
	8.4-8.8	160	19	¹ 6.5-8.0	1,300
	8.8-9.1	410		¹ 6.5-8.0	700
	9.5-10.2	740		8.0-9.0	570
	10.2-10.9	560		9.0-9.5	7.3
	11.0-11.8	32			
	11.8-12.5	7.1	20	6.7-7.5	810
				7.5-9.0	430
7	7.0-7.5	4.3		9.0-9.7	34
8	5.7-6.2	4.2	21	7.0-9.0	10
	7.0-7.5	4.6			
	7.5-8.0	1,200	22	6.3-7.5	870
	8.0-8.9	2,800		7.5-9.1	980
	8.8-9.5	12			
			23	7.3-8.3	13
12	7.8-8.8	9.8			
			24	6.5-8.0	960
13	7.8-8.8	8.5		9.5-11.0	56
14	7.5-8.3	32	25	(²)	8,8
	8.3-9.2	225			
			26	(²)	7.0
15	7.2-7.9	2,900			
	7.9-8.8	270	27	(²)	1,100
17	6.8-7.0	7.0	29	(²)	27
	7.0-8.0	1,300			
	8.0-9.2	220			

¹Duplicate (split) sample.

terrace and 5 percent of the total at hole 27 in the marsh. This indication of aromatic hydrocarbons in the subsoil makes their absence in ground water difficult to explain.

Possible Additional Source of Petroleum Contaminants

The appearance, transitorily, of less than 3 in. of hydrocarbon fuel floating in well 6 for a few months after its installation is puzzling. Furthermore, after being virtually absent for a year, a 6- to 8-inch layer of floating fuel again was observed in mid-1986, thus indicating the possible existence of another contaminant source in the vicinity of well 6.

Samples of floating hydrocarbon fuel were collected from wells 2 and 6 in May 1986 for comparison of physical properties. The sample from well 2 had a gasoline odor, but the sample from well 6 had a distinct odor reminiscent of diesel fuel in addition to the odor of gasoline. This contrasts with field observations in 1984-85 when no diesel-fuel odor was noticed. Specific gravity (at 23 °C) of the samples from wells 2 and 6, and of diesel fuel and unleaded gasoline purchased from a local service station, was measured to within an accuracy of 0.03. Specific gravity of the unleaded gasoline was found to be 0.68, about equal to the value of 0.69 for a sample from well 2; and specific gravity of the diesel fuel was found to be 0.78, close to the value of 0.76 for a sample from well 6.

Chemical differences between the free-floating hydrocarbon in wells 2 and 6 also are evident from GC-FID data that are illustrated in figure 9. Figure 9 is a graphical display of the relation between cumulative hydrocarbon-compound concentration and column-retention time on the gas chromatograph. In general, retention time (adsorption to the packed-column substrate) increases with decreasing compound volatility and increasing molecular weight. The gasoline standard is clearly more volatile than the diesel-fuel standard, with 90 percent of the gasoline and 10 percent of the

²Composite soil cuttings scraped off auger blades throughout contaminated interval.

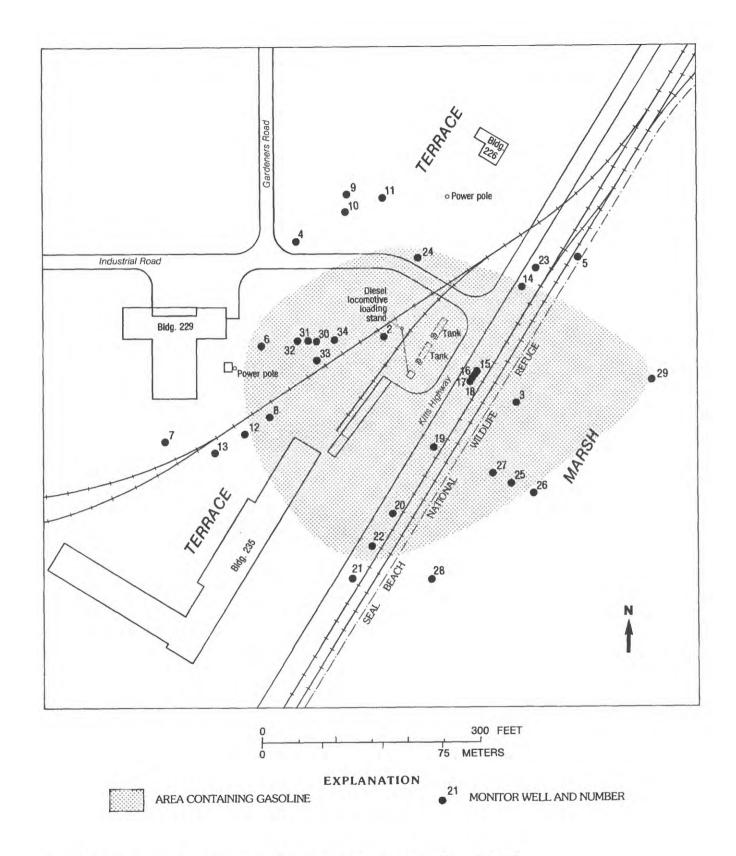


Figure 8. Estimated areal extent of gasoline plume in shallow subsoil.

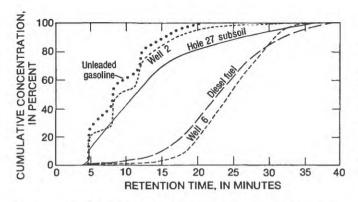


Figure 9. Distribution of retention times during gas-chromatographic analysis of fuel standards and hydrocarbons in the study area.

diesel fuel having retention times of less than 15 minutes by this method of analysis. This compares with 84 percent and 3 percent for wells 2 and 6, respectively. The gasoline standard and the hydrocarbon in well 2 also contain fewer compounds--about 100 with concentrations exceeding 0.1 percent, in comparison with 150 in the diesel-fuel standard and the hydrocarbon in well 6. Furthermore, nearly one-third of the gasoline standard and one-third of the hydrocarbon in well 2 are composed of three unidentified compounds having retention times near 5, 8, and 12 minutes: these three compounds make up only about 1 percent of the diesel fuel and 1 percent of the hydrocarbon in well 6.

The subsoil contains an even broader range of compounds than do the pure hydrocarbon phases. More than 200 compounds (each exceeding 0.1 percent of the total hydrocarbons) are distinguishable in the subsoil. Hydrocarbon composition in contaminated subsoil from the study area is intermediate between the extremes above, ranging from 10 percent with retention time less than 15 minutes at hole 22 to 75 percent at holes 27 and 29 in the marsh (composition for hole 27 is illustrated in fig. 9). However, it must be emphasized that these analyses cannot be used to apportion relative gasoline and diesel-fuel contribution at various

locations. Loss by evaporation, preferential adsorption of less-soluble compounds on mineral grains, and biodegradation will produce an enrichment of the higher-molecular-weight, less-volatile compounds in the subsoil--thus causing light-oil distillates (such as gasoline) to increasingly resemble medium-oil distillates (such as kerosene and diesel fuel) with time (weathering).

Schwille (1967) reported that gasoline infiltrates soil 1.5 times faster than water, and that, in contrast, the infiltration rate of diesel fuel is only 0.2 to 0.5 that of water. The changes in well 6 at Seal Beach may represent a lag in reestablishment of "equilibrium" conditions at this location. As much as 1 year was required for jet fuel to enter some wells in deposits at another location in Orange County (Ehrlich and others, 1987). Furthermore, leaks may have occurred intermittently in the past, and perhaps more than one source of contaminants was present in the study area. Further study would be necessary to determine with certainty if a second source of refined petroleum products existed within the study area. For practical purposes, the impact of contamination by either light- or medium-oil distillates is the same, and their behavior in the subsurface will differ little. especially after loss of volatile components and partial degradation.

Nitrate Concentration in Monitor Wells

Nitrate is thermodynamically unstable in an anaerobic (oxygen-free) environment, and microorganisms readily reduce nitrate in such environments. Since the gray band previously referred to suggests that degradation of gasoline in the study area has produced anaerobic conditions in the subsoil near the water table, it was anticipated that nitrate concentration would be lowest at monitor wells inside the identified area of the gasoline plume.

Results, which are illustrated in figure 10, show that NO₃-N (nitrate as nitrogen) concentration is several milligrams per liter in background wells outside the area of the plume and approaches the analytical detection limit of 0.1 mg/L in wells within the plume. Well 6 is the only exception: NO₃-N concentration was 1.6 mg/L. However, hole 6 was drilled to a depth of 26 ft below land surface, about 10 ft deeper than any other test hole was drilled and 15 ft below the contaminated subsoil. This may have brought oxygenated, nitrate-rich ground water and clean soils from uncontaminated deeper zones up closer to the surface where they did not yet have time to equilibrate with the contaminated zone prior to sampling (only 6 days elapsed between drilling and sampling).

Volatile Organic Compounds In Monitor Wells

Simple aromatic compounds such as benzene and methyl- and ethyl-substituted benzenes, which constitute several percent of refined gasoline were found (as noted) in subsoil from two test holes in the Seal Beach study area. Unpublished results of a study by the author at a remote location in Death Valley National Monument, where an unleaded-gasoline servicestation tank leaked in the late 1970's (Buono and Packard, 1982), showed that even after 5 years, ground water in that shallow unconfined aquifer still contained benzene and toluene concentrations exceeding 1,000 μ g/L as far as 2,000 ft downgradient from the source. Similar high concentrations were expected, but not found, at the Seal Beach site. In fact, the only volatile organic priority pollutant found (detection limit was 3 μ g/L) using the purge-and-trap GC-MS method was 1,2-dichloroethane.

Dichloroethane, which seems to be generally indicative of areas contaminated by leaded gasoline, was found in several monitor wells; concentrations ranged from 3.3 to 69 μ g/L (detection limit, 3 μ g/L). Data in table 4

indicate that 9 of 10 wells within the gasoline plume had detectable dichloroethane. For well 27, in which dichloroethane was not found, the detection limit (8.2 μ g/L) was much higher because of high background levels within the laboratory when this particular sample was analyzed; therefore, its presence could have been missed. Samples from three of four wells outside the area of the plume had no detectable dichloroethane. The lone exception, well 21, is just outside the southern edge of the gasoline plume. Perhaps dichloroethane migrates slightly faster than the gasoline and is thus an indicator of the leading edge of the plume.

Bromine- and chlorine-substituted organic compounds of low-molecular weight are additives to regular (leaded) gasoline, in which they serve as scavengers for lead in the combustion chamber. Bruell and Hoag (1984) reported that

Table 4. Dichloroethane concentration in monitor wells

[Concentration is in micrograms per liter; <, less than]

Well	N	0									.,			centration
3	, .													32
12	1													< 3.0
13	1													< 3.0
15														50
16	· .													69
17	1 .													10
18														34
19														11
21	1													39
25														. 5.8
26														. 3.3
27					è									< 8.2
28	1													< 3.0
29														21

¹Wells outside area of contaminated subsoil.

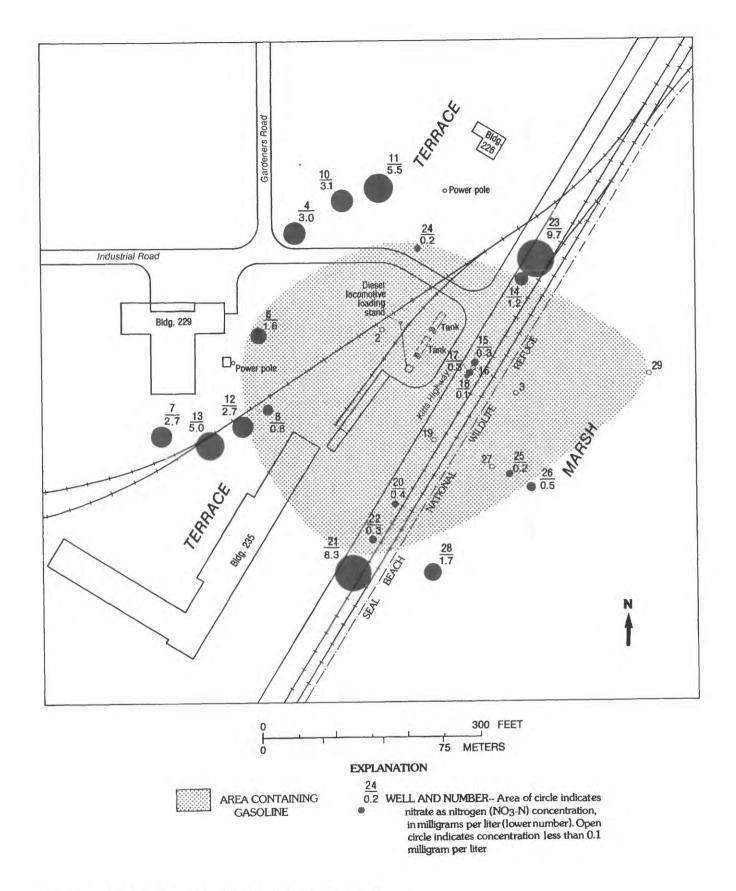


Figure 10. Nitrate concentration in monitor wells.

the concentration of 1,2-dibromoethane in leaded gasoline is about 0.03 percent and that 1,2-dichloroethane is present, but in lesser amounts. Water samples from Seal Beach were not analyzed for dibromoethane.

Estimated Quantity of Gasoline in the Subsoil

The quantity of hydrocarbon (weathered gasoline) absorbed on subsurface deposits can be estimated by multiplying its two-dimensional concentration, given in units of concentration per unit area, by the area contaminated. Subsurface gasoline per unit area (Q) at each test hole is calculated from the equation:

$$Q - \sum_{i} \rho_{i} c_{i} l_{i},$$

where ρ_i is the soil dry-weight bulk density (1.6 g/cm^3) , c; is hydrocarbon concentration (by GC-FID) per dry weight of soil, and l; is vertical length of the core (interval i) analyzed.

To apply the above equation, one must have hydrocarbon-concentration data for the entire contaminated part of the vertical profile.

Soil bulk density is estimated from the literature (Hillel, 1971) and from particle-size information in table 2 to be 1.6 g/cm³. Application of the above equation to GC-FID data in table 3 gives a range for subsurface gasoline per unit area of 0.64 to 1.53 kg/m²--except in the heavily contaminated central area near the leaky storage tank, and at well 6 (discussed in greater detail in later sections). Values calculated using data obtained from test holes outside the area of the plume are less than 0.01 kg/m², indicating that background hydrocarbon concentrations contribute less than 1 percent to calculated values within the area of the plume. Values calculated for each individual test hole on gas-chromatographic which hydrocarbon analyses were done are summarized in table 5.

The outer edge of the plume was delineated with great precision in some parts of the study area and only approximately in other parts. The net result is that maximum error in estimated area of contamination shown in figure 8 is 10 to 15 percent. Poorest delineation is in the northwestern part of the study area where the presence of roads, parking lots, fences, and buildings placed constraints on location of drilling sites. Best delineation was in the northeastern part of the study area in the marsh. Numerous shallow test holes (not indicated in the figures) were drilled between the railroad and hole 29 in the marsh until the leading edge of the plume was recognized by the presence of a very slight gasoline odor and small blebs of black or gray soil. Analyses shown in table 3 indicate that gasoline concentration in hole 29 is only about three times background concentration in holes 25 and 26, whereas interior parts of the contaminated area in the marsh (for example, hole 27) contain concentrations that exceed background by 100 times.

Table 5. Calculated areal concentration of gasoline at test holes

[kg/m², kilograms per square meter; <, actual value is less than value shown]

Hole	No.	Areal concentration of gasoline, rounded (kg/m²)								
6		10.5								
7		<.01								
8		1.5								
12		< .01								
13		< .01								
14										
15		1.1								
17		8								
18		8								
19		1.0								
20		6								
21		<.01								
22		1.3								
23		<.01								
24										

Results from a split core in one test hole and from cores in three adjacent test holes were used to ascertain error associated with the obtaining of the samples and with the processing of samples in the laboratory. A sample pair from each half of the split-spoon core at hole 19 gave hydrocarbon concentrations of 700 and 1,300 mg/kg (table 3). Calculated values of gasoline per unit area at holes 15, 17, and 18 (locations shown in fig. 3) are 1.11, 0.76, and 0.78 kg/m², respectively (table 5). All three test holes are within a few feet of one another and are in lithologically identical material. Therefore, precision is estimated to be about 30 percent.

Because no systematic spatial pattern of higher or lower gasoline-per-unit-area values was observed within the plume, except in the small region between the leaky storage tank and well 6 (implications discussed later), data from all test holes that are well within the area of contamination (except hole 6) were combined to yield a value of $0.98 \pm 0.31 \text{ kg/m}^2$. (Data from hole 14 was excluded from this calculation because hole 14 is very near the outer edge of the plume.) Note that the precision for this calculation matches the precision associated with sampling plus analytical errors discussed in the preceding paragraph. Total quantity of gasoline in the subsoil now can be calculated by multiplying areal concentration and the contaminated area of 160,000 ft2 (15,000 m²) and dividing by the specific gravity of analyzed hydrocarbons attached to the subsoil. Because no easy method exists to measure this specific gravity accurately, a published value of 0.675 for the specific gravity of gasoline (Weast and others, 1987) was selected. The published value is nearly identical to the measured value of 0.69 ± 0.03 measured for fuel floating in well 2.

From the information above, the estimated quantity of weathered gasoline contained in subsurface soils in the study area is 5,800 gal (22,000 L), with an uncertainty of about 2,000

gal. Implicit in this estimate is the assumption that gasoline per unit area is the same within the marsh as it is in the terrace. Although no values were obtained for the marsh, the similarity between measured hydrocarbon concentrations in hole 27 in the marsh and in test holes in the terrace, along with the similarity of visual appearance and odor of contaminated subsoil from test holes in the marsh and the terrace, would indicate that this assumption is valid.

The above calculation yields only a minimum estimate for the total quantity of weathered gasoline in subsurface soils, because the quantity of "free-floating" fuel in the heavily contaminated area between the leaky storage tank and well 6 was not determined. The only reliable way to determine the quantity in the heavily contaminated area would be through recovery. Analyses from test hole 6 show the quantity of hydrocarbon at hole 6 to be about 10 times greater than in other test holes within the plume (table 5). Thus, although the heavily contaminated area between the leaky storage tank and well 6 is small in comparison with the total area of the plume, it could contain as much as a few thousand gallons if this entire subarea were as heavily contaminated as it appeared to be at wells 2 and 6.

MIGRATION AND ASSIMILATION OF GASOLINE

Spreading of Gasoline in a Porous Medium

Downward movement of gasoline through a porous medium from a leaking tank is controlled by gravity plus capillary forces, and lateral movement is controlled by capillary forces. If the leak is sufficiently large to cause either the saturated or unsaturated flow of gasoline to the water table, the gasoline (because it is a water-immiscible fluid less dense than water) will begin to move laterally, forming a layer above the water table. Provided

that a concentration is maintained sufficient to cause further migration, the layer will continue to spread along the water table until the level of residual saturation (analogous to specific retention of water) is reached. At that concentration, lateral migration of the layer will cease.

Residual gasoline saturation, immobile gasoline saturation, and specific gasoline retention are terms used interchangeably in the literature (Schwille, 1967; van Dam, 1967; Dietz, 1971; McKee and others, 1972; and Fried and others, 1979). In this report the term "residual saturation" is used. As defined, residual saturation refers to the minimum gasoline concentration below which the gasoline will no longer migrate and is the quantity of gasoline being retained by capillary and molecular forces (against gravity). Residual saturation usually is expressed as a percentage of the pore (void) volume. Dietz (1971) used a residual saturation of 10 percent (pore volume) for oil hydrocarbons in a sand with porosity of 35 percent; van Dam (1967) used 10 to 20 percent depending on the grain size (residual saturation varies inversely with grain size); Fried and others (1979, fig. 1) showed a range from 19 to 27 percent, with higher values occurring when soil moisture content is low; and Fussell and others (1981) gave values of 7.5 percent for a coarse to medium sand, 12.5 percent for a medium to fine sand, and 20 percent for a fine sand and silt. McKee and others (1972), by saturating columns of sandy soil with gasoline and then allowing them to drain, determined that residual gasoline saturation for sandy soils ranged from 23.0 to 29.4 percent. They found that one column of dry soil with a porosity of 23.5 percent had a residual gasoline concentration (saturation) of 26 percent.

Residual hydrocarbon saturations are site specific and were not determined at the Seal Beach study area. However, approximate values of subsoil hydrocarbon concentrations can be calculated from available data at the Seal Beach study area and compared to residual

saturations taken from the literature and cited above. Data in table 3 indicate that the highest hydrocarbon concentration measured in subsoil from hole 6 is 3.2 percent of the dry mineral weight. Because the monitor well in this test hole initially contained fuel floating on the water, the subsoil is presumed to be at or above residual saturation. Hydrocarbon concentration as a percent of pore-void volume, Θ_s , is calculated by substitution into the following equation:

$$\Theta_S = \frac{\rho_S C_S}{\rho_G \Phi},$$

where

 ρ_S is dry-soil bulk density assumed to be 1.6 g/cm³,

 C_s is hydrocarbon concentration on dry-weight basis of 3.2 percent,

 ρ_G is hydrocarbon (gasoline) density of 0.675, and

is estimated subsoil porosity of
33 percent,

yielding a value of 23 percent. This number is close to values cited in the literature for residual saturation in fine sand and silt, suggesting that little further horizontal movement of hydrocarbon from the most heavily contaminated area would occur.

Additional evidence that subsoil concentrations within the heavily contaminated area near the leaky storage tank are close to residual saturation is provided by observations of thickness of the gasoline-contaminated subsoil during hand-augering of test hole 2. Thickness was estimated to be about 10 in., with gasoline concentration in subsoil above and below this interval clearly much less than within the 10-inch interval. This can be compared to a rough guide by Dietz (1971, table 1), which shows gasoline-thickness values of 11 in. for coarse silt, 9 in. for fine sand, and 6 in. for medium sand. Subsoil in the study area is mostly a silty fine sand (table 2 and fig. 4);

therefore, thickness of the gasoline layer at hole 2 is close to residual-saturation-thickness values quoted in the literature.

Maximum subsoil hydrocarbon concentrations in contaminated test holes outside the area between the leaky storage tank and well 6, where monitor wells contain no immiscible gasoline layer, are 0.1 to 0.3 percent (table 3; 1,000 mg/kg=0.1 percent), which is equivalent to about 1 to 2 percent of the pore volume. As expected, these concentrations are far below residual gasoline saturation, indicating that any further movement must be by transport in the vapor phase or with water. McKee and others (1972) found that when water levels were lowered and then raised in columns packed with gasoline-saturated soil, gasoline was spread vertically and its concentration was reduced below residual saturation. After the water level had been raised above the top of the soil column, no free gasoline floated on the water surface. At the Seal Beach study area, not even a thin layer of gasoline was present on the water in monitor wells within the contaminated area but away from the immediate area of the leak.

Thickness of the gasoline layer floating in well 2 was observed to range from 1 to 6 in. during nearly 2 years following installation of this monitor well. Although this is less than the expected thickness of subsoil containing gasoline at residual saturation in hole 2, thickness of the hydrocarbon-saturated zone in aguifer soils and the floating hydrocarbon liquid in wells are seldom equal for immiscible organic liquids (Villaume, 1985). As noted above, field observations of subsoil recovered during hand augering of hole 2 indicated that residual saturation thickness was about 10 in. at this location. The cause for temporal variations observed in thickness of the gasoline layer in well 2 is not known. Yaniga (1984) found that an inverse relation existed between gasoline-layer thickness

and ground-water altitude (greatest thickness when the water table was lowest) at several study sites. However, measurements were not made with sufficient regularity to establish a link between fluctuating ground-water levels and changing gasoline thickness in well 2 at Seal Beach. It is from wells with free-floating fuel, in areas where gasoline exceeds residual saturation in the soil, that cleanup of contaminated subsurface deposits by depression-pump skimming usually begins (de Postrovich and others, 1979, and Blake and Lewis, 1983).

Natural Assimilation of Gasoline in Subsoils

Schwille (1967) observed that heavy petroleum distillates and crude oil may persist for several decades, but there had been no case in which gasoline was retained in the subsoil for more than 10 to 15 years. The rapid disappearance of light fuel oils is attributed partly to volatilization of the low-molecular-weight components and substantially to biodegradation. Several bacterial species of *Pseudomonas* and *Arthrobacter*, genera that are ubiquitous in natural soils, were shown to be degrading gasoline at a major leak in the Los Angeles area (McKee and others, 1972).

Although biochemical transformations occur slowly in anaerobic environments, rapid and complete degradation requires the presence of molecular oxygen. Water, phosphorus and nitrogen nutrients, and trace elements also are essential. Nutrients, and especially oxygen, limit the degradation rate in most locations. Oxygen is replenished by precipitation and air diffusion. It is noteworthy that tidal fluctuations spread nutrients, water, and oxygen over a vertical zone of up to a few inches daily at the Seal Beach study area. For this reason, biodegradation may be much more rapid here than at most spill sites where water levels change infrequently in response to seasonal precipitation

patterns and oxygen is infused to the subsurface primarily during major storms, and where depth to ground water is greater. According to Dietz (1971), an oil pancake (layer) in the subsoil that is subjected to natural leaching by rainfall or accelerated leaching by artificial irrigation may lose its soluble components and gradually, over a period of years, be replaced by a predominantly paraffinic (alkanes) hydrocarbon pancake that will not move and is sparingly soluble. Absence of soluble aromatic compounds in all monitor wells located within the area of the gasoline plume suggests that this already might have happened at Seal Beach.

As noted in the introduction, the principal concern at Seal Beach is the potential for ecological damage to the marsh. Bioturbation by burrowing microorganisms, such as worms, can be a significant mechanism for exchange between surface water and interstitial water in subsurface muds. Such organisms require oxygen for respiration and obtain it by irrigating their tubes (burrows) with the surface water. Such replenishment of oxygen and nutrients could have the effect of enhancing in-place biodegradation by native microorganisms. Although the gasoline is only about 2 ft below land surface in the marsh, regular inundation by tides has compacted the intervening sediment between land surface and the contaminated subsoil beneath the marsh. Apparently, this provides an effective barrier to upward transport of contaminant: oil sheens have never been observed in surface water overlying the contaminated area; furthermore, the intervening sediment, although only about 2 ft thick, is uncontaminated.

SUMMARY AND CONCLUSIONS

Gasoline leaking from an underground storage tank has spread radially through the

shallow subsoil in an area of about 160,000 ft² on the U.S. Naval Weapons Station in Seal Beach, California, Contamination is largely confined to a zone about 1 to 2 ft thick near the water table. Results of this study, using GC-FID analyses of subsoil, indicated that the estimated quantity of hydrocarbon (weathered gasoline) contained in the subsoil, at concentrations below residual saturation, is 5,800 gal. with an uncertainty of 2,000 gal. The quantity contained in subsoil in the small heavily contaminated area near the leaky tank, where gasoline concentration exceeds residual saturation and is therefore potentially recoverable by pumping, was not determined but probably is less.

Although GC-FID analyses of subsoil samples were used to delineate the area and depth interval of the plume, several other surrogates that indicated the contaminated zone also were found. In the field, subsoil odor and color change (from oxidized brown to reduced gray as a result of microbial degradation) coincided with the presence of gasoline. Disappearance of nitrate (used during microbial degradation of hydrocarbon compounds) in ground water was found to be another tracer of contamination. Also, 1,2-dichloroethane (probably as an additive to gasoline) in ground water seems to be indicative of the presence of gasoline in the subsoil.

The hydrocarbon plume poses no threat to potable-water supplies because none exist near the study area. The major concern is the potential for ecological damage to a nearby marsh that serves as the Seal Beach National Wildlife Refuge. Although the gasoline is only about 2 ft below land surface in the marsh, laboratory analyses and field observations suggest that the compacted subsoil beneath the marsh provides an effective barrier to contamination of the surface water.

REFERENCES CITED

- Blake, S.B. and Lewis, R.W., 1983, Underground oil recovery: Ground Water Monitoring Review, v. 3, p. 40-46.
- Bruell, C.J., and Hoag, G.E., 1984, Capillary and packedcolumn gas chromatography of gasoline hydrocarbons and EDB, in Proceedings of the National Water Well Association and American Petroleum Institute Conference on Petroleum hydrocarbons and organic chemicals in ground water--Prevention, detection, and restoration, Houston, Texas, November 5-7, 1984: Worthington, Ohio, National Water Well Association, p. 234-266.
- Buono, Anthony, and Packard, E.M., 1982, Delineation and hydrologic effects of a gasoline leak at Stovepipe Wells Hotel, Death Valley National Monument, California: U.S. Geological Survey Water-Resources Investigations Report 82-45, 23 p.
- de Postrovich, T.L., Baradat, Y., Barthel, R., Chiarelli, A., and Fussell, D.R., 1979, Protection of ground water from oil pollution: The Hague, Netherlands, The Oil Companies International Study Group, CONCAWE Report no. 3/79, 61 p.
- Dietz, D.N., 1971, Pollution of permeable strata by oil components, *in* Hepple, Peter, ed., Water pollution by oil: Amsterdam, Elsevier, p. 127-139.
- Ehrlich, G.G., Schroeder, R.A., and Martin, Peter, 1985, Microbial populations in a jet-fuel-contaminated shallow aquifer at Tustin, California: U.S. Geological Survey Open-File Report 85-335, 14 p.
- ----1987, Microbial populations and nutrient concentrations in a jet-fuel-contaminated shallow aquifer at Tustin, California, in Ragone, S.E., and Sulam, D.J., eds., Program overview and selected papers from the Toxic-Waste Program Technical Meeting in Tucson, Arizona, March 20-22, 1984: U.S. Geological Survey Open-File Report 86-324, chap. G, p. 83-96.
- Feltz, H.R., Anthony, E.R., and Sadler, P., 1983, 1984 Water Quality Laboratory Services catalog: U.S. Geological Survey Open-File Report 83-758.
- Fishman, M.J., and Friedman, L.C., eds, 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, chap. A1, 545 p.
- Fried, J.J., Muntzer, P., and Zilliox, L., 1979, Ground-water pollution by transfer of oil hydrocarbons: Ground Water, v. 17, p. 586-594.

- Fussell, D.R., Gaedjen, H., Hayward, P., Lilie, R.H., Marco, A., and Panisi, C., 1981, Revised inland oil spill clean-up manual: The Hague, Netherlands, The Oil Companies International Study Group, CONCAWE Report no. 7/81, 146 p.
- Guy, H.P., 1969, Laboratory theory and methods for sediment analysis: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, chap. C1, 58 p.
- Hardt, W.F., and Cordes, E.H., 1971, Analysis of ground-water system in Orange County, California, by use of an electrical analog model: U.S. Geological Survey Open-File Report [71-145], 60 p.
- Hillel D., 1971, Soil and water--physical principles and processes: New York, Academic Press, p. 10-11.
- Ineson, J., and Packham, R.F., 1967, Contamination of water by petroleum products, *in* Hepple, Peter, ed., The joint problems of the oil and water industries: Amsterdam, Elsevier, p. 97-108.
- Keith, L.H., and Telliard, W.A., 1979, Priority pollutants I--a perspective view: Environmental Science and Technology, v. 13, p. 416-423.
- Lee and Ro Consulting Engineers, 1984, Soils investigation report, proposed fuel storage tank, U.S. Naval Weapons Station, Seal Beach, California: Job no. 84-135F, April 12, 1984, 14 p.
- McKee, J.E., Laverty, F.B., and Hertel, R.M., 1972, Gasoline in ground water: Journal of the Water Pollution Control Federation, v. 44, p. 293-302.
- Naval Energy and Environmental Support Activity, 1985, Initial assessment study of Naval Weapons Station, Seal Beach, California: Naval Energy and Environmental Support Activity Report no. 13-062, 8 chapters, 7 appendices.
- Schwille, Friedrich, 1967, Petroleum contamination of the subsoil--A hydrological problem, in Hepple, Peter, ed., The joint problems of the oil and water industries: Amsterdam, Elsevier, p. 23-54.
- U.S. Environmental Protection Agency, 1979, Guidelines establishing test procedures for the analysis of pollutants: Federal Register, v. 44, p. 69468-69483.
- van Dam, J., 1967, The migration of hydrocarbons in a water-bearing stratum, in Hepple, Peter, ed., The joint problems of the oil and water industries: Amsterdam, Elsevier, p. 55-88.
- Villaume, J.F., 1985, Investigations at sites contaminated with dense non-aqueous phase liquids (NAPLs): Ground Water Monitoring Review, v. 5, p. 60-74.

- Wall, J.R., Moreland, J.A., and Cordes, E.H., 1967, An investigation of potential salt-water intrusion from inland waterways in the shallow alluvial and coastal deposits of Sunset and Bolsa Gaps, Orange County, California: U.S. Geological Survey Open-File Report [67-151], 64 p.
- Weast, R.C., Astle, M.J., and Beyer, W.H., eds., 1987, CRC handbook of chemistry and physics, 68th edition: Boca Raton, Florida, CRC Press, p. F-3.
- Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., eds., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, chap. A3, 80 p.
- Whittemore, I.M., 1979, High resolution gas chromatography of the gasolines and naphthas, *in* Altgelt, K.H., and Gouw, T.H., eds., Chromatography in petroleum analysis, Chromatography Science Series, v. 11: New York, Marcel Dekker, p. 41-74.
- Yaniga, P.M., 1984, Hydrocarbon retrieval and apparent hydrocarbon thickness: Interrelationships to recharging/discharging aquifer conditions, in Proceedings of the National Water Well Association and American Petroleum Institute Conference on Petroleum hydrocarbons and organic chemicals in ground water-prevention, detection, and restoration, Houston, Texas, November 5-6, 1984: Worthington, Ohio, National Water Well Association, p. 299-329.